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STRUCTURE OF THE ELECTRONIC BANDS OF THE OD MOLECULE—PART II

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Plate III

ABSTRACT. In continuation of the work on the structure of the OD bands of heavy water, the (3,0) band at λ 2569 was photographed with a Hilger Quartz Spectrograph. An exposure of about 5 hours was found necessary on account of the faintness of the band. By an extrapolation of the existing data of the bands hitherto analysed, the rotational structure of this band was analysed. The values of the constants are found to be $B_3''=8.13$, $B_0'=9.94$ and the spin coupling constant $A=-139.6$ cms^{-1}.

INTRODUCTION

In an earlier paper,[1] the rotational structure of some of the electronic bands of heavy water, due to the diatomic molecule OD, were reported. A scrutiny of the plates taken with long exposures revealed the existence of a faint band at about λ 2570, the region in which the (3,0) band of OD corresponding to the band λ 2447 of the OH molecule must be expected. An examination of the rotational structure of this band confirmed the above supposition. The present paper gives details of the study of this band, a preliminary report of which has appeared in *Current Science*, 1940, 9, 368.

EXPERIMENTAL

The experimental arrangement for the excitation of the bands was already described in Part I. The faintness of this band made it impracticable to use an instrument of high dispersion; the band was therefore photographed with a Hilger medium Quartz spectrograph giving a dispersion of about 9 A.U. per mm. in the region λ 2570. With the time of exposure extending to about 5 hours, a picture of the band was obtained which could be conveniently measured, while the other bands were heavily over-exposed. The bands are reproduced in Plate I. The usual Iron Arc standards were adopted for the determination of the wavelengths. Due to the general faintness of the band and overlapping of the structure arising from the small dispersion of the instrument, the probable error in measurement is of the order of 0.1 to 0.2 A.U. Where the lines happened to be broad, the cross-wire was set in two or three positions—at the centre and at the edges. Such lines are indicated by asterisks in the list in Table I.

TABLE I

Int.	λ (obs.)	ν_{vac} (obs.)	ν_{vac} (calc.)	Classification					
				R_1	Q_1	P_1	R_2	Q_2	P_2
* 3	2569.1	38912	38913.6	2, 3	—	—	—	—	—
	69.4	908	909.7	1, 4	—	—	—	—	—
	69.6	904	903 8	5	—	—	—	—	—
2	70.1	896	895.5	6	—	—	—	—	—
3	71.2	880	882 7	7	—	—	—	—	—
			879.3	—	1	—	—	—	—
3	72.3	864	866.4	8	—	—	—	—	—
			865.4	—	2	—	—	—	—
			863 3	—	—	1	—	—	—
2	73.4	847	848.7	—	3	—	—	—	—
			847.1	9	—	—	—	—	—
3	74.4	831	832 9	—	—	2	—	—	—
			830.6	—	4	—	—	—	—
2	74 9	825	824.1	10	—	—	—	—	—
3	75.4	818	818.7	—	—	—	5, 6	—	—
			816.3	—	—	—	4	—	—
2	75.8	811	812.4	—	—	—	7	—	—
			809 2	—	—	—	3	—	—
3	76.3	803	806.4	—	5	—	—	—	—
			801.6	—	—	—	8	—	—
3	76.7	797	798.7	11	—	3	—	—	—
			796.9	—	—	—	2	—	—
2	77.5	786	786 8		—	—	9	—	—
3	77.9	779	781.6	—	6	—	—	—	—
			778 3	—	—	—	1	—	—
3	78.8	766	768 5	12	—	—	—	—	—
			768.1	—	—	—	10	—	—
			765.2	—	—	4	—	—	—

TABLE I (*contd.*)

Int.	λ (obs.)	ν_{vac} (obs.)	ν_{vac} (calc.)	Classification					
				R_1	Q_1	P_1	R_2	Q_2	P_2
			38752.7	—	7	—	—	—	—
			748.7	—	—	—	—	12	—
3	2580.0	38748	746.2	—	—	—	11	—	—
			744.7	—	—	—	—	3	—
			737.3	—	—	—	—	4	—
2	80.8	735	735.9	13	—	—	—	—	—
2	81.1	731	731.9	—	—	—	—	—	1
1	81.4	727	727.7	—	—	5	—	—	—
	81.8	721	722.3	—	—	—	—	5	—
			721.8	—	8	—	—	—	—
* 3	81.9	719	719.0	—	—	—	12	—	—
	82.0	717	716.2	—	—	—	—	—	2
2	82.9	704	704.8	—	—	—	—	6	—
2	83.7	692	694.7	—	—	—	—	—	3
			692.7	14	—	—	—	—	—
			687.5	—	—	—	13	—	—
	84.1	686	686.9	—	9	—	—	—	—
* 3			685.4	—	—	6	—	—	—
	84.4	682	682.4	—	—	—	—	7	—
2	85.1	671	671.9	—	—	—	—	—	4
2	86.1	656	657.0	15	—	—	—	8	—
2	86.7	648	652.8	—	—	—	14	—	—
			648.8	—	10	—	—	—	—
2	87.1	641	643.6	—	—	—	—	—	5
			641.8	—	—	7	—	—	—
2	88.1	627	626.6	—	—	—	—	9	—
			613.9	—	—	—	15	—	—
2	89.4	607	608.6	—	—	—	—	—	6
			607.2	—	11	—	—	—	—

TABLE I (*contd.*)

Int.	λ (obs.)	ν_{vac} (obs.)	ν_{vac} (calc.)	Classification					
				R_1	Q_1	P_1	R_2	Q_2	P_2
3	2590.3	38593	38594.2	—	—	8	—	—	—
			592 8	—	—	—	—	10	—
2	91.7	572	571.5	—	—	—	—	—	7
1	92.9	556	562.0	—	12	—	—	—	—
			554.6	—	—	—	—	11	—
1	93.8	541	544.0	—	—	9	—	—	—
1	94.6	530	529.4	—	—	—	—	—	8
1	95.8	512	512.8	—	13	—	—	—	—
			512.4	—	—	—	—	12	—
3	97.5	487	490.9	—	—	10	—	—	—
			483.8	—	—	—	—	—	9
2	99.0	465	467.8	—	—	—	—	13	—
			461.4	—	14	—	—	—	—
2	2601.1	433	434.9	—	—	—	—	—	10
			433.9	—	—	11	—	—	—
1	02.3	415	418.6	—	—	—	—	14	—
1	03.2	402	404.5	—	15	—	—	—	—
1	04.7	380	381.3	—	—	—	—	—	11
1	06.0	361	364 0	—	—	—	—	15	—
1	08.6	322	324.7	—	—	—	—	—	12
1	09 8	305	311.8	—	—	13	—	—	—
1	12.7	262	264 7	—	—	—	—	—	13
1	14.2	241	243.8	—	—	14	—	—	—
1	17.2	196	199.4	—	—	—	—	—	14
1	18.8	174	174.1	—	—	15	—	—	—

DISCUSSION AND RESULTS

As the rotational lines constituting the various branches of the band are not completely resolved, a method of extrapolation based on the previously known

data is adopted to predict and identify the structure. Considering the bands[2] (2,0) (3,0) and (2,1), (3,1) the interval between the $Q_1(1)$ lines of the (2,0), (3,0) bands is approximately equal to that between the corresponding lines of the (2,1), (3,1) bands, this interval being approximately equal to the difference between the initial vibrational levels $v'=2$ and $v'=3$, determined from the equation

$$G(v') = \omega'(v'+\tfrac{1}{2}) + x'\omega'(v'+\tfrac{1}{2})^2 + \ldots\ldots$$

Hence the position of the initial line $Q_1(1)$ of the (3,0) band is predicted. The positions of the other lines of this and those of the other branches are similarly located. The data thus predicted with respect to all the branches are collected and compared with the observed values and a consistent scheme of the structure of the band is developed. Table I gives the details of the intensity, the wavelength and other data of all the measured lines. Columns (3) and (4) show the observed and calculated values and the last columns give their assignments.

A check on the identification of the band is afforded by comparison of the doublet separations of the bands having the same final level, *i.e.*, (0,0), (1,0), (2,0) and (3,0). As an illustration, the doublet separations

$$Q_1(K) - Q_2(K)$$

and

$$P_1(K) - P_2(K)$$

for the above bands are given in Table II, in which the data for the (3,0) band have been obtained from the assignments shown in Table I (Column 3, ν observed).

TABLE II

K	$Q_1(K)-Q_2(K)$				$P_1(K)-P_2(K)$			
	λ 3065 (0,0)	λ 2872 (1,0)	λ 2708 (2,0)	λ 2569 (3,0)	λ 3065 (0,0)	λ 2872 (1,0)	λ 2708 (2,0)	λ 2569 (3,0)
1	131.4	131.0	131.1	132	131.	130·3	131.8	133
2	116.0	115.9	116.0	116	116.8	115·3	115.8	114
3	103.7	103.5	103.5	99	103.4	103.7	102.9	105
4	92.3	92.5	92.4	96	92.9	92.9	92.8	95
5	83.5	83.4	83.0	82	84.1	83 8	83.6	86
6	75.8	76.3	75.7	75	77.0	76.4	76.4	79
7	69.1	70.0	68.8	66	70.0	69.7	66.7	69
8	63.6	63.2	63.3	65	64.3	64.6	64.3	63
9	58.7	59.0	58.7	59	59.9	59.5	59.3	54
10	54 6	54.9	54.7	55	56.0	55.8	55.7	54
11	50.9	51.7	50.9	51	52.3	52.0	52.6	53
12	47.7	48.0	47.8	44	49.3	49.3	49.6	—
13	45.0	45.5	44.9	47	46.7	46.8	46.7	43
14	42.8	42.4	42.6	—	44.4	44.1	44.2	45
15	40.5	40.5	40.4	41	42.4	43.6	—	—

A further check on the correctness of the assignments is obtained by the application of the combination relations shown below and already referred to in detail elsewhere.[1] It can be easily seen that

$$R_1(K)-P_1(K)=\triangle_2F'_1(K)$$
$$R_2(K)-P_2(K)=\triangle_2F'_2(K).$$

The difference between the values $\triangle_2F'_1(K)$ and $\triangle_2F'_2(K)$ may be ignored on account of the small spin-doubling in the upper $^2\Sigma^+$ state. Table III gives the values of $R_1(K)-P_1(K)$ and of $R_2(K)-P_2(K)$ for the (3,2), (3,1) and (3,0) bands.

TABLE III

Rotational term differences for the $^2\Sigma^+$ state

K	$R_1(K)-P_1(K)$			$R_2(K)-P_2(K)$		
	λ 2963 (3,2)	λ 2756 (3,1)	λ 2569 (3,0)	λ 2963 (3,2)	λ 2756 (3,1)	λ 2569 (3,0)
2	81.4	80.3	81	81.9	79.7	80
3	114.2	113.6	115	114.7	112.0	119
4	144.5	144.6	142	144.5	144 0	147
5	177.4	176.7	177	176.4	176 0	177
6	208.8	208.8	210	208.1	208.5	211
7	240.1	240.4	239	239.2	240.1	239
8	272.2	271.4	271	271.3	271.5	273
9	302.8	302.8	306	302.6	302.6	299
10	333.6	333.6	338	333.4	333.5	333
11	364.9	364.8	364	363.1	364.4	368
12	394.1	394.5	—	—	—	—
13	424.0	424.6	430	—	424.1	424
14	—	454.2	451	—	455 8	452
15	—	483.5	482	—	—	—

The table confirms that the band at λ 2569 corresponds to the initial level $v'=3$.

The combination relations involving the lower $^2\Pi$ state are contained in the equation,

$$R(K-1)-Q(K)=Q(K-1)-P(K).$$

It must be noted that the equation is only approximate, the difference between the two sides being a measure of the Λ-doubling in the rotational levels.

Tables IV and V show the values of the above differences. The values in columns (3) and (5) in these tables are obtained from the observed values of the lines in Table I. Columns 2 and 4 contain the values estimated from the bands (0,0), (1,0) and (2,0). The data indicate the correctness of the assignment of the band λ 2569 as arising from the final state $v''=0$

TABLE IV

K	$Q_1(K-1)-P_1(K)$		$R_1(K-1)-Q_1(K)$	
	Estimated mean for bands (0,0), (1,0), (2,0)	Observed for λ 2569 (3,0)	Estimated mean for bands (0,0), (1,0) (2,0)	Observed for λ 2569 (3,0).
2	46.6	49	46.2	44
3	65 0	67	65.0	65
4	83.7	81	84.1	81
5	102.1	104	102.9	105
6	120.9	117	122.0	125
7	140.0	138	141.2	148
8	158.9	155	160.2	159
9	177 6	180	179.3	178
10	196.1	199	198.4	199
11	214.8	215	217.2	218
12	233.2	-	236.5	241
13	251.3	251	255.3	254
14	269 5	271	274.1	270
15	287.0	291	293.0	290

TABLE V

K	$Q_2(K-1)-P_2(K)$		$R_2(K-1)-Q_2(K)$	
	Estimated mean for bands (0,0), (1,0), (2,0)	Observed for λ 2569 (3, 0)	Estimated mean for bands (0,0), (1,0), (2,0)	Observed for λ 2569 (3,0)
2	31.4	31	31.8	31
3	52 5	56	52.1	49
4	73.0	77	72.9	76
5	93.5	94	92.2	97
6	114 2	114	113.8	114
7	133.9	132	133.4	136
8	154 0	152	153.5	155
9	173.8	169	173.3	176
10	193.2	194	193 2	193
11	212.3	213	212.3	210
12	231.4	234	231.8	236
13	250.2	250	250.8	254
14	268.6	269	270.1	271
15	—		288 8	287

The final check consisted in estimating the values of the rotational constants B_3' and B_0'', the method of calculating them being that previously adopted by the author for the bands λλ 2872, 2916 and 2963. The values of these constants are found to be $B_3' = 8.13$ and $B_0'' = 9.94$ cms.$^{-1}$. They are in good agreement with those observed previously, *i.e.*, $B_3' = 8.074$ from the (3,1) band and $B_0'' = 9.927$ from the (1,0) band. The spin-coupling constant is found to have a mean value -139.6 cms.$^{-1}$.

Table VI is an extension of that given in Part I showing the vibrational analysis of the OD-bands. For each band the calculated value of the null line is inserted in the table, the value for the (3,0) band being determined from the present data.

TABLE VI

Null lines of the OD-bands $^2\Sigma^+ - {}^2\Pi_{\frac{3}{2}}$

v' \ v''	0		1		2
0	ν 32542.29	—	—	—	—
	2215.9	—	—	—	—
1	34757.3	—	—	—	—
	2112.1	—	—	—	—
2	36869.4	2632.7	34236.7	—	—
	2007.7	—	2008.0	—	—
3	38877.1	2632.4	36244.7	2541.2	33700.5

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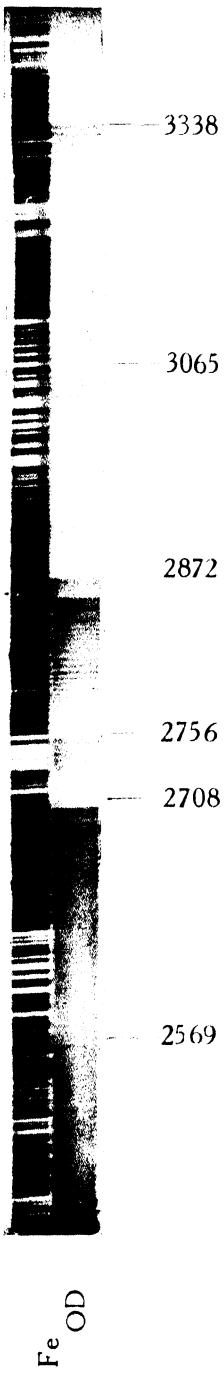
REFERENCES

1 M. G. Sastry and K. R. Rao, *Ind. J. Phys*, **15**, 27 (1941).

2 The data quoted in this paper for the bands (0,0), (2,0) and (3,1) are due to Ishaq, *Proc. Roy. Soc.*, **159**, 110 (1937) and *Proc. Nat. Inst. Sc. Ind.*, **3**, 389 (1937) and those for (1,0), (2,1) and (3,2) are due to the author and K. R. Rao, *ibid.*


3338
3065
2872
2756
2708
2569
Fe OD